NASA TECHNICAL TRANSLATION NASA TT F-12,679

NASA TT F-12,679

THE REACTIVITY OF SODIUM CHLORATE

E. Osada, K. Kusamoto and K. Mukai

Translated from "Kogyo Kayaku Kyokaishi," Vol. 27, No. 2, pp. 91-100, 1966.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 NOVEMBER 1969

NASA TT F-12,679

THE REACTIVITY OF SODIUM CHLORATE

E. Osada, K. Kusamoto and K. Mukai[1]

ABSTRACT. We studied on the reactivity of $NaClO_3$ from the view points of the thermal decomposition reaction, and the reactions of $NaClO_3$ with H_2SO_4, HCl, and some organic compounds.

The thermal decomposition occurs at about 440°C. At first $NaClO_3$ decomposes into NaCl and O. This O atoms react with undecomposed $NaClO_3$, producing $NaClO_4$. On the other hand, NaCl accelerates the decomposition of $NaClO_3$. The reaction equations for this mechanism are as follows; $NaClO_3 \rightarrow NaCl + 3O. 3O + 3NaClO_3 = 3NaClO_4$, (overall reaction: (a) $4NaClO_3 \rightarrow 3NaClO_4 + NaCl$) and $NaCl + NaClO_3 \rightarrow 2NaCl + 3O$ (overall reaction: (b) $NaClO_3 \rightarrow NaCl + 3O$). The molar ratio of the reaction (a)/(b) is varied with temperatures, and the maximum value of the ratio is 75/25 at 520°C. When $NaClO_3$ is completely decomposed at 530°C, the ratio (a)/(b) is 67/33, and overall reaction equation is $2NaClO_3 \rightarrow NaClO_4 + NaCl + O_2$. This autocatalytic decomposition reaction of $NaClO_3$ has the activation energy of 49 kcal. Above 540°C, $NaClO_4$ which is the decomposition product of $NaClO_3$, decomposes into NaCl and $2O_2$ according to the one half order reaction, and its activation energy is 70.5 kcal.

The catalytic effect of NaCl on the decomposition of $NaClO_3$ is only detected with the chemical analysis of the reaction products and is not clearly observed from its weight loss.

Ignition reaction of $NaClO_3$-organic compounds occurs at the melting point of $NaClO_3$, and the activation energies were obtained as 30 ~ 50 kcal from the measurements of induction periods.

The reaction of $NaClO_3$ with H_2SO_4 occurs according to the equation of $3ClO_3^- + 2H_2SO_4 = ClO_4^- + 2ClO_2 \uparrow + 2HSO_4^- + H_2O$. But on the reaction of $NaClO_3$ with HCl, a simple

[1]Received February 18, 1966. The Kyushu Institute of Technology, Tobata-ku, Kitakyushu City.

reaction equation is not obtained because the ratio ClO_2/Cl_2 is varied with the concentrations of HCl and $NaClO_3$.

Since $NaClO_3$ absorbs moisture slightly, it is not a desirable raw material for explosives. In recent times, it has come into broader use as a raw material for forming ClO_2 and as a weed killer but its stability has created problems. For the purposes of the present report, a study was made of the thermal decomposition reaction of $NaClO_3$ by chemical analysis and X-ray diffraction. The results of this study and tests of this compound's reactions with several acids as well as its reactivity when intermixed with organic substances were made and are covered below. /29[1]

Experiments and Analytical Methods

The tests of the thermal reactivity of $NaClO_3$ and its thermal behavior were by differential thermal analysis, while the measurements of weight loss were made with a thermo-balance. The identification of the decomposition products was based on ASTM standards and was based on X-ray diffraction. For the purposes of the chemical analysis of the products, $AgNO_3$ was used for the NaCl, while $FeSO_4$, $(NH_4)_2SO_4$ was used for the $NaClO_3$. For the determination of the quantity of $NaClO_4$ formed, the sum of the total of the NaCl and $NaClO_3$ present in the product was subtracted from the total quantity of the decomposition product, concurrently with which comparative tests were made in which a determination of $NaClO_4$ was accomplished in accordance with the JIS method[1]. To give an example, the quantity of $NaClO_4$ as determined from the weight reduction at 520°C was 0.0344 grams while the quantity as determined by the JIS method was 0.0397 grams, these results being relatively consistent. On the basis of the fact that the presence of $NaClO_4$ was confirmed during the classification by X-ray analysis, the calculated values were used to compute the quantity of $NaClO_4$, and the quantity of O_2 generated was determined from the weight reduction.

The analysis of the Cl_2 and the ClO_3, which was formed during the reactions between $NaClO_3$ and H_2SO_4 and HCl was made by absorbing these substances in the gaseous phase in neutral potassium iodide solution, then determining the total Cl by titration with a $Na_2S_2O_3$ solution. The KI solution was then made

[1]Received February 18, 1966.

acidic and the ClO_2 determined. Cl_2 was calculated from the difference. The determination of ClO was by making the test solution alkaline and titrating with As_2O_3 using KI as the indicator.

Deducing Decomposibility by Calculation

Meyer, M. Markowitz [2], and their collaborators made a study of the thermal decomposition of the alkaline metal chlorides. They determined that the rapid decomposition temperatures were as follows: 376°C for $LiClO_3$, 465°C for $NaClO_3$, 472°C for $KClO_3$, 480°C for $RbClO_3$ and 483°C for $CsClO_3$. They observed the presence of Li_2O in the decomposition products of $LiClO_3$ but pointed out that chlorides are formed by the other salts. In the case of this decomposition reaction, it is possible to make a general inference of decomposibility from Fajans' [3], concepts, the fact that the reaction progresses less readily as a function of increased metal ion diameter, and taking into consideration as well, polarity or the potential between the bonds. Further, as it had been determined that errors develop as a result of thermal stability at the formation temperature of the oxides or the chlorides that are among the reaction products, it is generally held that chlorides form with a reduction in the positive charge of the metal ion. It has further been generally recognized that $MClO_4$ is formed during the decomposition of $MClO_3$ and that this finally changes to MCl. Thus, decomposition equations which might be considered for $NaClO_3$ were established. The free energy change was determined as a function of temperature and the reaction process considered in this light. The values used in these calculations were those given in Table 1, while the values used for ΔH_{298} and ΔG_{298} were Latimer's values [4].

TABLE 1. THERMODYNAMIC PROPERTIES OF MATERIALS

Substance	C_p	ΔH_{298} kcal/mole	ΔG_{298} kcal/mole
NaCl	$10.79+0.00420\,T$	−98.232	−91.785
$NaClO_3$	$9.48+0.0468\,T$	−85.73	−60.746
$NaClO_4$	29.4	−92.18	−61.40
O_2	$6.5+0.0010\,T$	0	0

Calculations of the ΔG temperature changes using these values are as follows:

$$4NaClO_3 \rightarrow 3NaClO_4 + NaCl \qquad (1)$$
$$\Delta G_1 = -41,925.8 - 61.070T \ln T + 352,978T + 0.0915T^2$$

$$2NaClO_3 \rightarrow NaClO_4 + NaCl + O_2 \qquad (2)$$
$$\Delta G_2 = -23,290.6 - 27.73T \ln T + 116.64T + 0.0442T^2$$

$$3NaClO_3 \rightarrow 2NaClO_4 + NaCl + \frac{1}{2}O_2 \qquad (3)$$
$$\Delta G_3 = -32,608.2 - 44.4T \ln T + 232.809T + 0.0679T^2$$

$$NaClO_3 \rightarrow NaCl + \frac{3}{2}O_2 \qquad (4)$$
$$\Delta G_4 = -9,317.6 - 11.06T \ln T - 0.367T + 0.0201T^2$$

$$NaClO_4 \rightarrow NaCl + 2O_2 \qquad (5)$$
$$\Delta G_5 = -4,655.5 + 5.61T \ln T - 117.373T - 0.00310T^2$$

The correlation between ΔG and T is as shown in Figure 1. If it is given that the temperature changes in the specific heat of $NaClO_4$ are not great, reaction (5) will occur less readily than reaction (4) at temperatures below 330°K whereas reaction (5) will occur more readily than reaction (4) above 330°K.

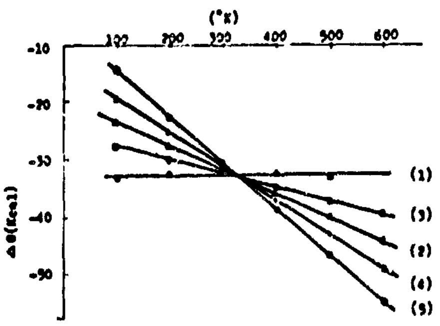

Figure 1. Thermodynamical Calculations of Various Reactions.

(1) $4NaClO_3 \rightarrow 3NaClO_4 + NaCl$
(2) $2NaClO_3 \rightarrow NaClO_4 + NaCl + O_2$
(3) $3NaClO_3 \rightarrow 2NaClO_4 + NaCl + 1/2O_2$
(4) $NaClO_3 \rightarrow NaCl + 3/2O_2$
(5) $NaClO_4 \rightarrow NaCl + 2O_2$

However, as the results of the differential thermal analysis of $NaClO_2$, $NaClO_3$ and $NaClO_4$, as given in Figure 2, show, $NaClO_4$ is stable at high temperatures and this trend is not proportional to the reduction in ΔG. To compare these three compounds, $NaClO_2$ undergoes a violent exothermic decomposition reaction in the vicinity of 150°C, forming $NaClO_3$. The $NaClO_3$ melts in the vicinity of 260°C, then undergoes exothermic decomposition at 450°C, forming $NaClO_4$. This $NaClO_4$

undergoes exothermic decomposition in the vicinity of 530°C and forms NaCl. Thus, decomposition follows the route $ClO_2^- \rightarrow ClO_3^- \rightarrow ClO_4^-$ and it may be observed that all of the salts and chlorides are finally formed. $NaClO_4$ is more stable than $NaClO_3$. On the basis of the changes in ΔG, reaction (5) tends to occur more readily within the high temperature region, however since ΔG represents potential, it is mandatory that the effects of chemical resistance must be taken into consideration, since resistance has an effect on reaction velocity during the reaction process. The Cl-O bond is the same in all of these salts. The negative electrical charge of Cl is 3.0 while that of O is 3.5, [5] thus, the electrons between Cl-O are drawn towards the O side and the Cl electron shows a plus quality. If it is given, as a result, that the Cl atom becomes Cl^- as the final product, then the Cl in ClO_3^- is reduced from +5 to -1, and the Cl in ClO_4^- is reduced from +7 to -1, the O ion is oxidized into a neutral atom and the Cl-O bond is broken. Thus, since resistance represents the restorability of the bonding electron between Cl and O, this becomes a question of the potential of the unit electron. In reaction (4), since the six electrons between Cl and O move from O to Cl, and eight electrons move the same way in reaction (5), ΔG may be divided by this number and consideration given to the potential of eight electrons. In Figure 1, at 600°K, ΔG_4 = -49 kcal and ΔG_5 = -54 5 kcal. If it is then given that V is the potential per unit electron, then the value in equation (4) becomes -8.2 kcal, and -6.8 kcal in equation (5), thus (4) > (5) and reaction (4) will occur more readily at high temperatures than reaction (5).

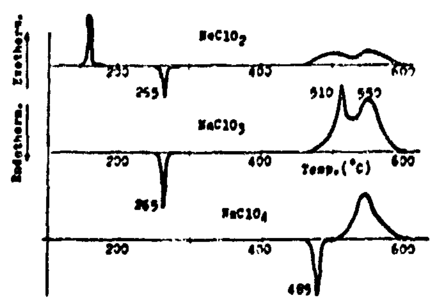

Figure 2. Differential Thermal Analysis of $NaClO_2$, $NaClO_2$ and $NaClO_4$.

Since ClO_4 is recognized as an intermediate product in the decomposition of ClO_3, it may be considered that the O atom, which is formed when the Cl-O bond in the $NaClO_3$ molecule is broken, is captured by the $NaClO_3$ to oxidize it and form $NaClO_4$. The greater stability of $NaClO_4$ at high temperatures suggests the occurrence of $NaClO_3 + O \rightarrow NaClO_4$. If it is then considered that the bonding energy of the three Cl-O bonds in $NaClO_3$ are equal, one $NaClO_3$ will (a) enter into an excitation state during the decomposition process in which $NaClO_3 \rightarrow NaCl+3O$ placing the Cl-O bond in a "loose" state, the O atoms then move towards the neighboring, inactive $NaClO_3$ to form $NaClO_4$. As a result (b) the reaction $3O+3NaClO_3 \rightarrow 3NaClO_4$ may occur. From (a) + (b), apparently, the previously given equation (1) $4NaClO_3 \rightarrow 3NaClO_4+NaCl$ obtains. On the other hand in the case of the case of the uncaptured O atom, only reaction (a) takes place and the thermal decomposition reaction of $NaClO_3$ may be as Markowitz has pointed out. The parallel reaction (1) $4NaClO_3 \rightarrow 3NaClO_4 + NaCl$ and (4) $NaClO_3 \rightarrow$ $\rightarrow NaCl + \frac{3}{2}O_2$. Further, as pointed out earlier, the reaction equations (2) and (3) represent a combination of the above reactions (1) and (4). In reaction equation (2), 1.33 moles of the 2 moles of decomposing $NaClO_3$ will react as in equation (1) and 0.67 moles as in equation (4). In reaction equation (3) of the total of 3 moles of $NaClO_3$ that decompose, 2.67 moles react as in equation (1) and 0.33 moles as in equation (4). This indicates that equation (2) and (3) may be derived as the overall reaction equation. That is to say, in equation (2) 67% reacts in accordance with decomposition equation (1) and 89% reacts that way in equation (3). A number of decomposition equations have been suggested in the past and the differences in the molar ratios of these reaction equations may be attributed to consideration of special cases in which equation (1) was considered alone and when it was considered in combination with (4).

Thermal Decomposition Reactions

I. X-Ray Analysis

As it was inferred from Figure 2 that $NaClO_4$ is formed during the thermal /31 decomposition of $NaClO_3$, $NaClO_3$ was heated at specified temperatures, cooled and subjected to X-ray analysis and the products classified in accordance with the ASTM standards, in order to confirm this thesis [6].

H. Coapaux [7], has stated that there are four forms of $NaClO_3$ (1) cubic (2) unstable, rhombic crystalline (3) monoclinic crystalline and (4) pseudo-cubic crystalline. However, the samples were of the cubic form as specified in ASTM. Figure 3 shows the X-ray patterns for the reaction product of NaCl,

$NaClO_3$ and $NaClO_4$ after heating to 480°C, 520°C and 540°C in 5 minutes. Figure 4 gives the same results for $NaClO_3$. On the basis of the X-ray patterns, no decomposition of $NaClO_3$ was observed at 480°C, the presence of NaCl and $NaClO_4$ was observed at 520°C, while virtually all of the $NaClO_4$ disappeared at 540°C and only NaCl appears. Thus, NaCl and $NaClO_4$ are formed during the thermal decomposition of $NaClO_3$ subsequent to which the $NaClO_4$ is decomposed, and only NaCl remains as a solid substance following the decomposition of $NaClO_4$. The above results are consistent with the previous theory that $NaClO_4$ is formed during the decomposition of $NaClO_3$ following which it itself decomposes.

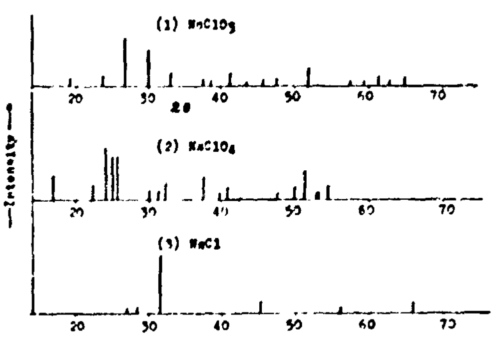

Figure 3. X-Ray Patterns of $NaClO_3$ $NaClO_4$ and NaCl.

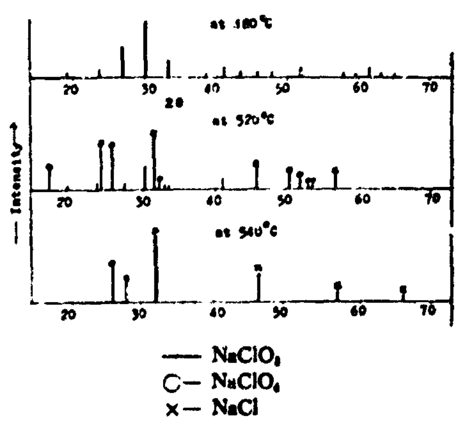

Figure 4. X-Ray Patterns of $NaClO_3$ Heated at Various Temperatures.

II. Chemical Analysis

a. Decomposition Reaction During Heating.

In order to obtain the mass balance an analysis was made of the decomposition products identified in the section above in experiments conducted with the normal methods. The quantity of $NaClO_4$ was determined by subtracting the total quantity of NaCl and undecomposed $NaClO_3$ from the total residue. The weight reduction was determined by measuring the O_2. The results obtained were as given in Figure 5 and Table 2. Decomposition is observed beginning in the vicinity of 460°C. The ratio, $Na/NaClO_4$ shows a higher quantity of NaCl in the low temperature region, however, conversely, the formation of $NaClO_4$ increases beyond 500°C. There are almost equal molar quantities present in the vicinity of 530°C. The decomposition of the $NaClO_4$ formed begins beyond 530°C with the quantity of NaCl formed increasing as this process takes place giving a reaction $NaClO_4 \rightarrow NaCl + 2O_2$. This suggests that the decomposition equation for $NaClO_3$ is, as stated before, a parallel reaction of reactions (1) and (4).

TABLE 2. DECOMPOSITION PRODUCTS OF $NaClO_2$ (mole %)

Temp (°C) / Products	440	460	480	500	520	530	540	560	580	630
$NaClO_3$*	2.7	6.3	12.3	18.8	82.3	87.3	92.9	96.1	98.6	100.0
NaCl	2.5	3.7	7.3	10.4	35.7	43.8	47.9	78.7	89.8	99.6
$NaClO_4$	1.5	2.7	6.6	8.8	46.3	44.5	43.2	15.9	8.0	0.0
O_2	1.5	3.8	7.2	9.7	31.3	40.1	56.4	118.2	137.7	150.4

$NaClO_3$*: mole % of Decomposition

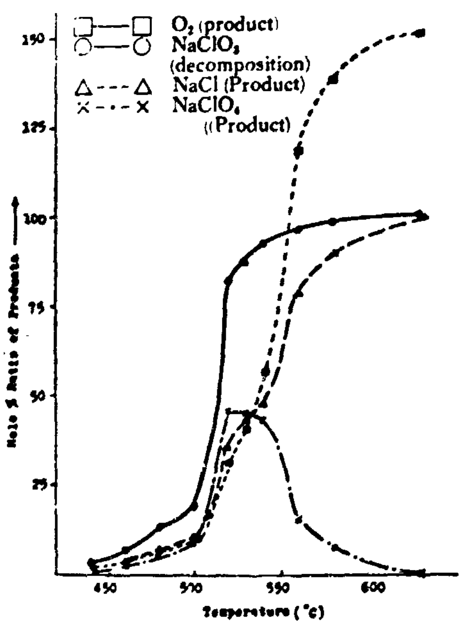

Figure 5. Chemical Analysis of $NaClO_3$ Decomposition Heating Rate 5°C/min.

Further, as Figure 5 clearly shows, /32 the principal reaction in the vicinity of 540°C is reaction equation (5), $NaClO_4 \rightarrow NaCl + 2O_2$. To consider, next, the reaction equations in the low temperature region of $xNaClO_3 \rightarrow 0.75xNaClO_4 + 0.25xNaCl$ and $yNaClO_3 \rightarrow yNaCl + 1.5yO_2$, where the quantity of $NaClO_3$ decomposed = x + y, the quantity of NaCl formed = 0.25x + y, the quantity of $NaClO_4$ = 0.75x and the quantity of O_2 formed = 1.5y. These values were calculated for each one of the temperature ranges, to give the correlation between x and y as shown in Table 3.

As a result of the above calculations, there is a proportional increase in reaction (1) with elevations in the temperature which reaches 75% in the vicinity of 520°C. There is an apparent reaction equation, $16NaClO_3 \rightarrow 9NaClO_4 + 7NaCl + 6O_2$. This reaction subsequently drops reaching 67% at 530°C. The overall reaction equation at 530°C is equivalent to $2NaClO_3 \rightarrow NaCl + NaClO_4 + O_2$. As the temperatures are elevated further, the $NaClO_4$ which is formed in reaction (1) begins to decompose as in equation (5). At 580°C about 64% of the product of the reaction in (1), $NaClO_4$, has decomposed as in reaction equation (5). It can be observed as shown in Figure 5 that 100% has decomposed at 630°C.

TABLE 3. RATIO OF REACTIONS (%)

Reaction \ Temperature (°C)		460	480	500	520	530	540	560	580
$4NaClO_3 \rightarrow 3NaClO_4 + NaCl$	(1)	60	65	65	75	67	64	50	47
$NaClO_3 \rightarrow NaCl + 1.5O_2$	(4)	40	35	35	25	33	32	25	23
$NaClO_4 \rightarrow NaCl + 2O_2$	(5)						4	25	30

b. Fixed Temperature Decomposition Reaction.

The results of making measurements with a constant temperature and varied times, with the reaction at 480°C, were as given in Table 4. Table 5 shows the ratios between the reaction equations.

TABLE 4. DECOMPOSITION PRODUCTS OF $NaClO_3$ (mole %, AT 480°C)

Product \ Time (min)	2	3	5	8	10	15	22	30	40	50	60
$NaClO_3$*	3.4	8.0	14.0	34.5	49.0	71.6	92.3	94.3	95.2	95.5	96.0
NaCl	2.5	4.0	7.4	15.0	21.0	31.4	46.0	46.7	49.8	59.0	62.0
$NaClO_4$	0.9	4.0	6.6	19.1	26.2	39.7	45.1	47.8	44.9	35.6	33.2
O_2	3.6	3.9	7.9	14.1	20.7	28.9	45.9	46.4	54.2	73.7	79.2

$NaClO_3$*: mole % of Decomposition

TABLE 5. % OF RATIO OF REACTIONS (AT 480°C)

Reaction \ Time (min)		2	3	5	8	10	15	22	30	40	50	60
$4NaClO_3 \rightarrow 3NaClO_4 + NaCl$	(1)	35	66	63	73	76	74	67	67	66	60	64
$NaClO_3 \rightarrow NaCl + 1.5O_2$	(4)	65	34	36	27	24	25	33	33	33	30	32
$NaClO_4 \rightarrow NaCl + 2O_2$	(5)									1	10	14

As Table 5 shows, reaction (4) takes precedence during the very early period for about 4 minutes, however, with the passage of time the O atom which is formed is captured by the unreacted $NaClO_3$. The ratio of reaction (1) increases proportionately and reaction (1) finally assumes about a 75% role. This role gradually decreases and the overall reaction becomes $2NaClO_3 \rightarrow NaClO_4 + NaClO_2$. There is, then, an induction period of about 20 minutes (22-40 minutes) in which the decomposition of the $NaClO_4$ formed begins. By 60 minutes, approximately 21% of the $NaClO_4$ that had been formed in reaction (1) has decomposed. Markowitz holds that reaction (1) attains a maximum of 67%, however, in the course of the present experiment, reaction (1) reached 75%. /53

Table 6 shows the decomposition product at 350°C.

TABLE 6. DECOMPOSITION PRODUCTS OF $NaClO_3$ (mole %) AT 530°C

Time (min) / Products	3	5	7	9	11	13	16
$NaClO_3$*	90.1	92.9	94.5	95.6	96.4	97.1	97.9
NaCl	45.2	52.4	66.2	71.0	75.7	79.0	84.4
$NaClO_4$	42.8	38.0	24.0	19.5	16.4	15.2	9.4

$NaClO_3$* mole % of Decomposition

Decomposition was rapid at 530°C making it impossible to measure the quantity of O_2. The difference between the reaction at this temperature and that at the low temperature range was that virtually no induction period was noted in the formation of $NaClO_4$, which immediately decomposed.

c. The Effects of NaCl on $NaClO_3$.

As a means of studying the catalytic activity of the NaCl formed on the $NaClO_3$, 1 mole of NaCl was added per 5 moles of $NaClO_3$ and a determination made of the product. The data derived are given in Table 7 together with the ratios of the $NaClO_3$ decomposition reaction.

The results show that the NaCl accelerates the decomposition of $NaClO_3$ and increase the quantity of $NaClO_4$ formed. Specifically, the reaction $NaClO_3 + NaCl \rightarrow 2NaCl + 3O$ is accelerated and a large quantity of oxygen is formed at the same temperature. The quantity of the oxygen atoms captured by the undecomposed $NaClO_3$ is also great and the ratio of the reaction $3O + 3Na + 3NaClO_3 \rightarrow 3NaClO_4$ increases. There is, however, virtually no change in the quantity of O which remains diffused outside of the system in an uncaptured state. Thus, it is virtually impossible to observe any effects in tests of the autocatalysis of NaCl with the weight reduction method, however, autocatalysis was clearly evident when the chemical analysis method was applied. Insofar as the reaction mechanics are concerned, during the initial period the reaction $NaClO_3 \rightarrow NaCl + 3O$ occurs, immediately following which the following reaction takes place.

TABLE 7. DECOMPOSITION PRODUCTS OF $NaClO_3$ (mole %) AND RATIO OF REACTIONS (%)

Product \ Substance / Temp (°C)	$NaClO_3$				$NaClO_3$ (5) : NaCl (1)			
	460	510	515	530	460	510	515	530
$NaClO_3$*	6.2	28.1	41.9	88.7	21.8	63.6	77.7	92.6
NaCl	3.9	11.8	20.0	45.0	9.3	25.0	27.7	46.7
$NaClO_4$	2.3	15.9	22.1	43.8	13.7	39.3	50.6	45.5
O_2	3.7	11.2	13.7	55.1	3.8	15.7	14.1	48.6
$4NaClO_3 \rightarrow 3NaClO_4 + NaCl$	50	76	70	66	78	81	86	66
$NaClO_3 \rightarrow NaCl + 1.5O_2$	50	24	30	34	22	19	14	34

$NaClO_3$*: mole % Decomposition

$$+)\ 3O + NaClO_3 \rightarrow 3NaClO_4$$

$4NaClO_3 \rightarrow 3NaClO_4 + NaCl$. About 67% of the decomposed $NaClO_3$ participates in this O capturing reaction, indicating that of the three O atoms generated, two are captured and one remains diffused outside of the system. Further, autocatalysis, in which the NaCl that is formed accelerates the reaction of $NaClO_3$ in the reaction $NaClO_3 + NaCl \rightarrow 2NaCl + 3O$ takes place. When NaCl is added, the $NaClO_4$ formation reaction reaches a maximum of 86% producing an overall reaction $3NaClO_3 \rightarrow 2NaClO_4 + NaCl + 0.5O_2$. Of the nine O atoms, eight are captured by the $NaClO_3$ and one remains free.

III. The Reaction Rate Equation

As stated earlier, there is an autocatalysis type of reaction during the /34 initial reaction period in the decomposition of $NaClO_3$. At just about the time the $NaClO_3$ has decomposed, there is a short induction period and the $NaClO_4$ formed decomposes. As a means of identifying the rate determining step in the above reactions that take place during the initial period, the $NaClO_4$, NaCl and O_2 formation rates at 480°C were calculated using the values shown in Table 4. It is believed that the formation rate of $NaClO_4$ represents the reaction rate for the reaction $NaClO_3 \rightarrow NaClO_4$ and that the rate of O and NaCl formation principally represents the reaction rate in reaction $NaCl + NaClO_3 \rightarrow 2NaCl + 3O$.

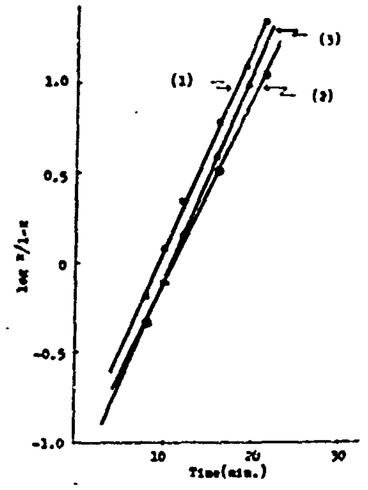

Figure 6. Log x/1 - x~t at 480°C. (1) $NaClO_4$, (2) NaCl, (3) O_2

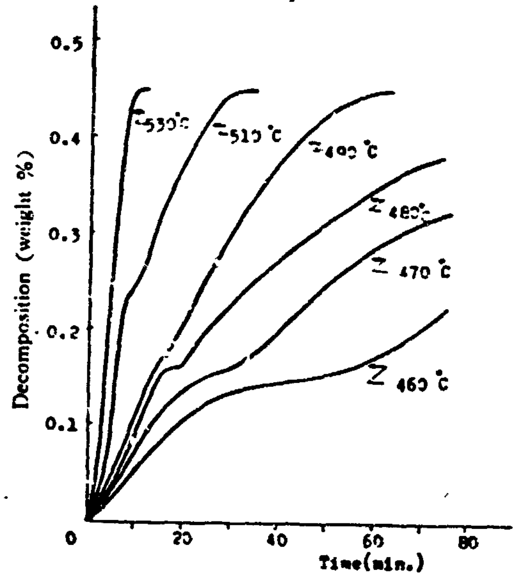

Figure 7. Decomposition Rate of $NaClO_3$ at Various Temperatures.

The autocatalysis equation $dx/dt = kx(1-x)$ is fully applicable for determining the NaCl, $NaClO_4$ and O_2 formation rates during the initial period of the reaction up to 22 minutes. The relationship of $\log \frac{x}{1-x} \sim t$ is given in Figure 6.

The formation rate constants for $NaClO_4$, NaCl and O_2 are, respectively, 0.25/min., 0.23/min and 0.27/min. These are almost equal and demonstrate that the previously described reaction is of the parallel type. Accordingly, it is possible to determine the rate for the overall reaction by measuring the O_2 formed.

Figure 7 shows the correlation between the weight loss (the quantity of O_2 generated) and time at the various temperatures. Within the low temperature range, the reaction is clearly divided into two steps. The first stage reaction ends when about 16% of the total weight has decomposed following which the second stage decomposition reaction takes place with the reaction terminating with the decomposition of about 45% of the starting substance. As indicated earlier, the reaction velocity during the first stage is of the autocatalysis type $\frac{dx}{dt} = kx(1-x)$ while a 1/2 order rate equation $\frac{dx}{dt} = k(1-x)^{1/2}$ can be derived for the second stage. In the above, x is the reaction rate for each stage. /35

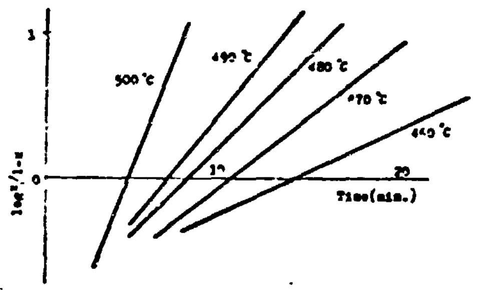

Figure 8. log x/1 - x ≈ t at Various Temperature. (First Step Reaction).

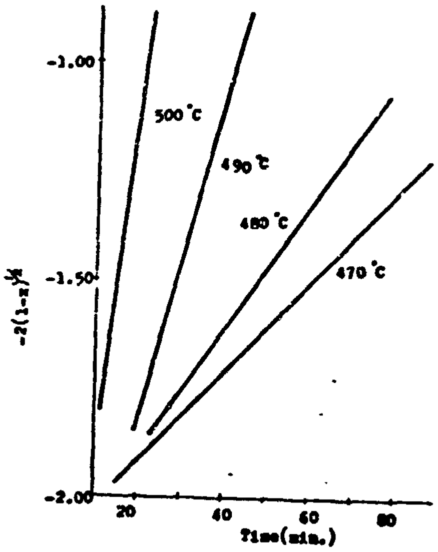

Figure 9. $-2(1-x)^{1/4}$ ≈ t at Various Temperature. (Second Step Reaction).

Figures 8 and 9 show the correlation between time and the integrals of the reaction rates at each stage. There is a linear correlation in all cases, the rate constant k at each temperature is derived from the gradient of the line and the apparent energy of activiation then derived from log k ~ 1/T. This gives a value of 48.9 kcal/mole for the first stage and 78.5 kcal/mole for the $NaClO_4$ decomposition reaction during the second stage. Thus, the O_2 formation reaction, which takes place during the initial reaction period, takes place more readily than the O_2 formation reaction during the second stage.

IV. Reactions in Mixed Systems

As there has been an increase in recent years in the use of $NaClO_3$ as a weed control in forests, tests were made with the intent of determining the dangers in mixing this compound. The means used was to measure the thermal reactivity with various organic materials by differential thermal analysis and measurements of ignition time. The results of the differential thermal analysis were as given in Figure 10.

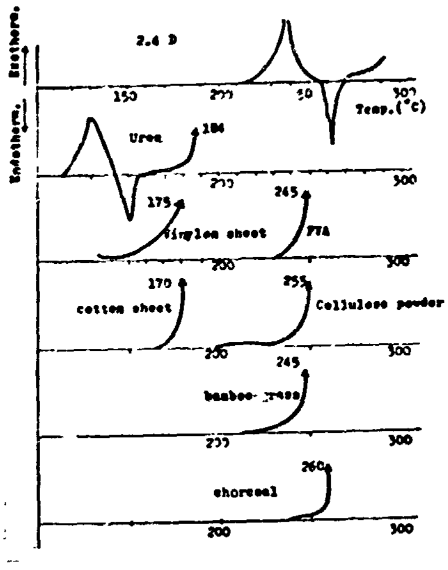

Figure 10. D.T.A. of the Mixtures of $NaClO_3$ and Organic Substances.

The weed killer, 2-4-D ignites in the vicinity of the $NaClO_3$ melting point of 240°C. Urea in a simple mixture ignites in the vicinity of 190°C. As these reactions occur below to the melting point of $NaClO_3$, caution in preparing organic mixtures is required. Vinylon and cotton cloth impregnated with about 20 weight per cent of $NaClO_3$ ignited at 170-180°C. The ignition point, in contrast, of powdered mixtures with PVA and Avicel was in the vicinity of 250°C. Further, an ignition reaction occurred in the vicinity of 250°C in mixtures with powdered bamboo grass leaves and wood charcoal. The temperature around 250°C is that at which $NaClO_3$ melts. Specifically, from these examples, it was noted that the movement of the O in $NaClO_3$ in the vicinity of 150°C takes place within the solid and is a solid phase contact surface reaction with materials that have high oxidizability while, when temperatures are raised still further, the bonds between the molecules are weakened by melting and an ignition results immediately.

The next tests were made to determine the apparent activation energy required to cause ignition. These organic substances were prepared in simple mixtures with $NaClO_3$ and the time required before ignition was measured. The ignition temperature was taken as that with a delay time of five seconds. The results obtained are shown in Table 8. The energy of activation was high in those mixtures in which the organic substances melted during combustion, then decompose. The values were almost equal to the energy of activation during the first stage of the $NaClO_3$ decomposition reaction. The ignition temperature of vinylon is particularly high. The ignition reaction occurs subsequent to the melting and decomposition of the vinylon causing the ignition point to slip towards the high temperature side. Accordingly, in the apparent ignition suppression of the $NaClO_3$ type weed killers, one might consider the addition of substances which show an endothermic reaction during melting or decomposition before the ignition point, or the addition of substances which will control the reaction deriving from the transition in the $NaClO_3$ melting phenomenon by forming eutectic mixtures with $NaClO_3$, or by adding inert substances.

TABLE 8. ACTIVATION ENERGY CALCULATED FROM IGNITION DELAY

Substance	Ignition Temperature °C	Actiation Energy Kvcal/mole
Cotton	249	58.5
PVA	403	49.3
Chlorophyll	272	42.9
lignin	289	27.8
Charcoal	292	26.9
tea leaves	266	47.0
bamboo grass	272	45.7

V. Reactions With Acids

V.1 Reactions with H_2SO_4.

In recent years $NaClO_3$ has been used as the starting material for the bleach, ClO_2. Owing to the fact that an explosion reaction takes place when $NaClO_3$ comes in contact with highly concentrated H_2SO_4, the following tests were made of the reaction mechanism.

A suitable quantity of H_2SO_4 was dripped into an equeous solution of $NaClO_3$ at 30°C. The gas which was generated was bubbled into a KI solution, the Cl_2 and the ClO_2 gas were determined from the liberated I_2. An analysis was made of the reaction solution to determine the Cl^- and the ClO_3^-. The ClO_4^- was calculated from the Cl material balance. There was no ClO^- present. If it is given that the quantity of $Na_2S_2O_3$ is V_1cc when titration with a $Na_2S_2O_3$ solution with the reaction $2KI + Cl_2 \rightarrow 2KCl + I_2$, $KI + ClO_2 \rightarrow KClO_2 + 1/2I_2$ in a neutral KI solution, and that the quantity of liberated I_2, when the solution is made acidic and the reaction $KClO_2 + 4KI + 2H_2SO_4 \rightarrow KCl + 2K_2SO_4 + 2H_2O + 2I_2$ occurs in V_2cc, the number of moles of Cl_2 is $= \frac{1}{2}(V_1 - \frac{1}{4}V_2)$, /36
and the number of moles of ClO_2 is $= \frac{1}{4}V_2$. When a determination is made of ClO_3^- and Cl^- by the normal method, the quantity of Cl, which is derived by subtracting the total ClO_3^- and Cl^-, and the total gaseous Cl, are subtracted from the Cl in the known reagent $NaClO_3$. The Cl ca be calculated as that in the ClO_4^- which remains in the aqueous solution.

Table 9 shows the analytical results one hour after the reaction time at a temperature of 30°C.

TABLE 9. REACTION PRODUCTS OF $NaClO_3$-H_2SO_4
(1hr, 30°C)

Experimental number		1	2	3
H_2SO_4(18mole/l)cc		25	30	15
(A)$NaClO_3$($\times 10^{-3}$mole)		5.75	5.75	5.75
Solution	$NaClO_3$ ($\times 10^{-3}$mole)	0.80	0.56	3.07
	ClO_2^- ($\times 10^{-3}$mole)	0.0	0.0	0.0
	Cl^- ($\times 10^{-3}$mole)	0.0	0.0	0.0
Gas	ClO_2($\times 10^{-3}$mole)	3.25	3.34	1.71
	Cl_2($\times 10^{-3}$mole)	0.086	0.09	0.05
(B) Total Cl		4.22	4.08	4.88
(A)−(B)=(C) ClO_4^- ($\times 10^{-3}$mole)		1.53	1.67	0.87
ClO_2/(C)		2.12	2.00	1.97
Reaction ClO_3^-/(C)		3.24	3.11	3.08
Reaction ClO_3^-/product ClO_2		1.53	1.55	1.56

On an average, two moles of ClO_2 are formed for each one mole of $NaClO_4$, three moles of $NaClO_3$ are formed for each one mole of $NaClO_4$ formed, while two moles of ClO_2 are formed for each three moles of $NaClO_3$. Since there is about 2-3% of Cl_2 of the ClO_2, this is disregarded and it is believed that the reaction equation is the following. $3ClO_3^- + 2H_2SO_4 \rightarrow ClO_4^- + 2ClO_2 + 2HSO_4^- + H_2O$. Accordingly, it is suggested that the H_2SO_4 causes the following reaction with ClO_3^-; $3ClO_3^- \rightarrow ClO_4^- + 2ClO_2 \uparrow + O^{--}$. Since it is held that an explosion will occur if there is about 10% of ClO_2 itself in the atmosphere, particular care is required in handling when a reducing agent is present.

V.2 Reaction with HCl

Measurements were made with Cl_2 and ClO_2 by the previously described analytical method when a specified concentration of HCl was added in a small quantity to a $NaClO_3$ solution and the gas that was formed was absorbed in a KI solution. The HCl concentrations were varied between 0.59 N, 1.49 N and 8.19 N. This compound was added to a saturated aqueous solution of $NaClO_3$ at 30°C to cause the reaction. The results obtained were as shown in Figure 11. The formation of ClO_2 gas is marked with H_2SO_4 in concentrations on the order of 24 N, while formation of ClO_2 was noted at much lower concentrations of HCl. Another point of difference with H_2SO_4 was that the quantity of Cl_2 was very close to the quantity of ClO_2 formed. As the Figure shows, the ratio ClO_2/Cl_2 nears one as the concentration of HCl is increased. Additionally, the high quantity of the gas formed during the period of initial contact may be attributed to a temporary increase in the reaction velocity resulting from the localized accumulation of reaction heat. Since ClO_2 is a strongly acidic gas, and even though the explosiveness of the ClO_2, itself, may be attenuated by the Cl_2, caution is required when a reducing substance is present. Further, if an acid salt is present as an impurity in the $NaClO_3$, it may be considered that HCl may be formed by minute quantities of adhered water. This creates the possibility of the previously described decomposition reaction occurring. Therefore, caution is required when a heavy metal salt is mixed in.

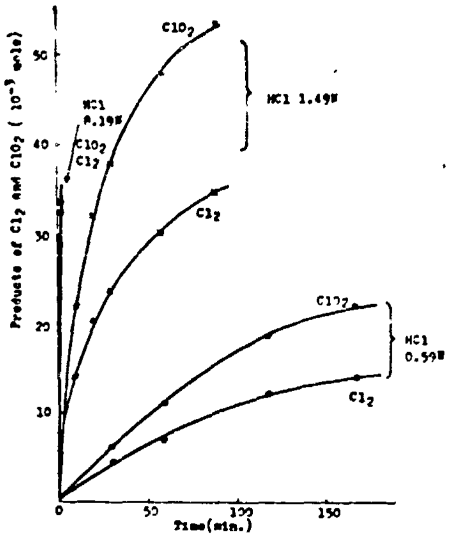

Figure 11. Reaction of $NaClO_3$-HCl
$NaClO_3$ (30°C, Saturated Solution 20 cc) HCl 10 cc, Reaction Temperature 30°C.

Next, in order to establish these reaction equations, a determination was made of the material balance before and after the reaction by making an analysis of the quantity of gas generated and the reaction solution at a temperature of 30°C for 30 minutes, to give the results shown in Table 10. As the Table makes evident, the consumption and production of the total Cl throughout the reaction is consistent. Thus, there is no ClO^- or ClO_4^- in the reaction products. It was observed that the reaction products were ClO_2, Cl_2 and Cl^-. Since there is a difference in the ratio between ClO_2 and Cl_2 as a function of differences in the quantity of HCl and ClO_3^-, it is evident that there is a complex reaction between HCl and $NaClO_3$ making it difficult to establish a reaction equation. If it is given that the reaction equation is $aNaClO_3 + bHCl \rightarrow mClO_2 + nCl_2 + pNaCl + qH_2O$, $a + b = m + 2n + p$ for the Cl, $a = b$ for the Na, $b = 2q$ for the H, and $3a = 2m + q$ for the O. If the values m, n, p and q are represented as a and b from equation 4, then

$$a\mathrm{NaClO_3} + b\mathrm{HCl} = \frac{6a-b}{4}\mathrm{ClO_2} + \frac{5b-6a}{8}\mathrm{Cl_2} + a\mathrm{NaCl} + \frac{b}{2}\mathrm{H_2O}$$

TABLE 10. REACTION PRODUCTS OF $NaClO_3$-HCl (at 30°C, 30 min.)

Before Reaction			After Reaction					ClO_2/Cl_2
ClO_3^-	HCl	Total Cl (10^{-3} mole)	ClO_2	Cl_2	ClO_3^-	Cl^-	Total Cl	
50.94	43.28	94.22	5.94	3.85	44.95	35.63	94.22	1.54
5.56	23.79	29.35	0.54	0.69	4.80	23.53	30.25	0.78

VI. Conclusions

The following conclusions may be drawn from the above experimental results.

(1) The thermal decomposibility of $NaClO_2$, $NaClO_3$ and $NaClO_4$ increases in that order. During the decomposition process, the following stable products are formed as intermediates, $NaClO_2 \rightarrow NaClO_3 \rightarrow NaClO_4 \rightarrow NaCl$. There is, thus, a final conversion to NaCl.

(2) The thermal decomposition reaction of $NaClO_3$ falls into two stages as a function of temperature. In the low temperature ranges in the vicinity of 530°C, there is (a) a reaction $NaClO_3 \rightarrow NaCl + 3O$ and a continuing reaction between a slight number of the O atoms that are formed and the unreacted $NaClO_3$, i.e., $NaClO_3 + O \rightarrow NaClO_4$ and (b) the reaction $4NaClO_3 \rightarrow 3NaClO_4 + NaCl$ to give two parallel reactions, (a) and (b). There are variations in the molar ratios in the $NaClO_3$ decomposition equation as a function of proportions between reactions (a) and (b). The oxygen capturing reaction increases as a function of increases in the temperature and the overall reaction at the maximum value which is attained at 530°C is $2NaClO_3 \rightarrow NaClO_4 + NaCl + O_2$. During the process of this reaction, the NaCl that is formed acts to accelerate the decomposition of the undecomposed $NaClO_3$. Thus, there are three parallel reactions: $NaClO_3 \rightarrow NaCl + 3O$, $NaCl + NaClO_3 \rightarrow 2NaCl + 3O$ and $NaClO_3 + O \rightarrow NaClO_4$. At 530°C the reaction, $NaClO_4 \rightarrow NaCl + 2O_2$, involving the formed $NaClO_4$ occurs. Thus, the initial reaction is an autocatalytic reaction.

(3) It is difficult to measure the autocatalytic effects of the NaCl on the $NaClO_3$ by the reduction in weight method, however, it is possible to make a determination of the result by a chemical analysis.

(4) The initial $NaClO_3$ reaction conforms to the autocatalytic type $\frac{dx}{dt} = kx\ (1-x)$, the energy of activation is 48.6 kcal/mole. The second stage reaction is a 1/2 order reaction and $\frac{dx}{dt} = k\ (1-x)^{1/2}$ applies. In the latter case the energy of activation is 70.5 kcal/mole.

(5) In the great majority of the mixtures with organic matter, the reaction shifts into the ignition type concurrently with a melting of $NaClO_3$.

(6) The reaction with sulphuric acid follows the form $3ClO_3^- + 2H_2SO_4 \rightarrow$